

Continuous-Filament Casein Yarn*

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Abstract

A process for producing continuous-filament casein yarn by pot-spinning is described. The fiber has a tensile strength of 1.0–1.2 grams per denier, elongation of 50 percent, excellent softness, and warmth. Fiber evaluation indices are presented.

ARTIFICIAL PROTEIN FIBER would be expected to have unique properties as a continuous-filament yarn. Its warmth, softness, hand, and range of colors with acid dyes would give the textile designer a new material for use in both woven and knitted goods. With these ideas in mind, studies on the development of continuous-filament casein yarn were initiated in 1945. The process developed is reported in this paper. It is closely related to the staple-fiber process reported previously [8], but major modifications were required to increase the rate of hardening and to prevent adhesion between the filaments.‡

Equipment and Test Methods

The equipment used (Figure 1) was essentially that described in the previous publication, with the addition of a rayon centrifuge pot operating at either 3,600 or 5,000 r.p.m. A ventilating hood has been added to the machine since the photograph was taken, for the removal of formaldehyde vapor given off by the treatment bath.

Denier was determined by weighing 9 cm. of the yarn on a micro-torsion balance. Tenacity and elongation were determined by breaking 2-inch gage lengths of these 9-cm. samples on a Scott I-P-2 Serigraph. Dry tests were carried out at 70°F and 65 percent relative humidity. Wet tenacity was de-

termined after the weighed samples had been soaked for ½ hour in individual test tubes of distilled water. Ten tests were averaged in each case. The fiber evaluation indices proposed by Smith [10] were calculated from these data. Stiffness of the tow was determined in an arbitrary manner. A number of pieces of yarn were mounted in parallel in an Olsen-Tour-Marshall 0.5-inch-pound model stiffness tester, and the resistance to bending was measured.

Work recovery was determined on single filaments by a single-fiber autographic tester [11]. The area under the recovery curve divided by the area under the extension curve, expressed as a percentage, is the work recovery for any selected elongation.

Experimental Procedure

The major steps in the new process are: (A) preparation of the spinning solution, (B) spinning it into a precipitating bath, (C) simultaneous stretching and treating in a heated stretch bath, (D) adjusting the pH in a treatment bath, (E) collecting the tow in the centrifuge pot, (F) storing, washing, and drying the cake, and (G) stabilizing the fiber by after-treatment. Each step has been investigated in considerable detail.

(A) The casein solutions were prepared from a high-quality acid-precipitated commercial casein. The casein was mixed with sufficient water and sodium hydroxide to produce a 25-percent solution having a pH of 7. It was then heated to 55°C with constant stirring, and stored overnight at this temperature to deaerate. Phenyl or pyridyl mercuric acetate of 0.025-percent concentration was added in the water as a preservative. These and similar salts are

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‡ Application for a public service patent has been made.

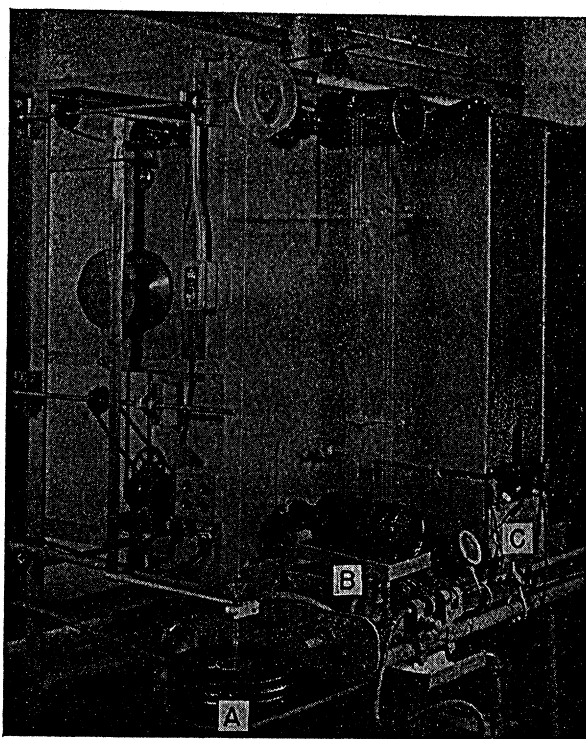


FIG. 1. Apparatus for spinning continuous-filament casein yarn. A—Rayon-type centrifuge. B—Treatment bath. C—Stretch bath; upper cone godet only is visible.

excellent preservatives in this pH 7 solution. The usual spinning viscosity was 500–600 poises at 25°C.

(B) The highly acid precipitating baths previously employed have been replaced by an acetic acid bath. The new bath enables fine filaments to be spun more readily, for it permits a greater rate of draw-off from the precipitating bath, and there is also less acid carry-over to the stretch bath. Table I gives data which show the composition of the two baths and the effects produced.

TABLE I. COMPOSITION OF PRECIPITATING BATH VERSUS TOW PROPERTIES

Composition	pH	% Casein in tow*	Max. draw ratio†
10% H ₂ SO ₄ , 22% Na ₂ SO ₄	0.2	30	1.9
6% HOAc, 20% Na ₂ SO ₄	3.5	38	3.9

* Determined by centrifuging skeins to get the wet weight. To get the dry casein weight, the same skein was hardened in formaldehyde to make it insoluble, washed, dried, and weighed.

† Calculated from jet extrusion rate; spinneret 250 0.003-diameter holes; extrusion at 5.4 ml./min.

(C) The stretch bath employed contained 10 percent sodium sulfate, 10 percent aluminum sulfate, and 5 percent formaldehyde. The cone godets previously described were used. The lower one was partially immersed in the stretch bath, which was maintained at a definite temperature. A stretch of 100 percent, which absorbed the tendency of the fiber to sag under the treatment, was imposed on the tow by these cones, and additional stretch was introduced after this treatment as the fiber was taken to the next godet wheel. The time of treatment in the stretch bath was approximately 2 minutes.

An increase in tenacity quite similar to that obtained previously with the sulfuric acid baths was observed. (See Table II.)

When the fiber was collected in the centrifuge pot immediately after this treatment, it was stiff and "plastered" together, owing to incomplete hardening. However, two chemical effects of importance occurred during this treatment: formaldehyde and aluminum ion were taken up. The formaldehyde content of the tow coming out of the stretch bath was 2.0 percent, but only 0.5 percent was bound firmly enough to resist washing with water. A reasonable increase in time of treatment in the bath did not increase the percent of bound formaldehyde enough to make this a practicable hardening treatment. About 0.5 percent of aluminum is introduced by the stretch bath. This fact was taken advantage of to produce a supplementary hardening effect in the next step.

(D) The fiber was passed through a concentrated (30-percent) sodium acetate bath at pH 6. This treatment presumably precipitates a basic aluminum

TABLE II. INCREASE IN TENACITY BY STRETCHING TO MAXIMUM IN HEATED SALT-CH₂O BATH, FOLLOWING ACETIC-ACID PRECIPITATING BATH*

Temp. of bath (°C)	Max. obtainable stretch (%)	Tenacity at 70°F, 65% R.H. (g./den.)	Wet tenacity (g./den.)
27	145	0.71	0.26
35	190	0.78	0.27
45	215	0.83	0.32
55	280	0.93	0.40
65	400	1.03	0.43
75	530	0.95	0.46
60	428	1.2	0.56

* Except in the last line of the table, data were obtained at a jet extrusion rate of 4.73 meters a minute, and a take-off speed of 9.15 meters per minute. By lowering the take-off speed to 6.25 meters per minute, the time of contact with the bath is increased, and a higher stretch may be imposed at 60°C.

TABLE III. IMPROVEMENT IN FLEXIBILITY OBTAINED BY USE OF TREATMENT BATH

No.	Treatment	No. filaments/denier	Stiffness* in in.-lbs. $\times 10^4$
1	No wash bath	250/400	23.
2	Wash at pH 5	250/400	16.
3	Wash at pH 6	250/400	1.6
—	Commercial viscose yarn, oiled for knitting	100/300	1.6

* Arbitrary units, obtained by mounting fibers in parallel in an Olsen-Tour-Marshall 0.5-in.-lb. model stiffness tester.

salt on the surface of the fiber. The individual filaments no longer adhere. The twisting of the tow as it enters the centrifuge does not stiffen it, and the layers of yarn in the cake do not stick. Moreover, the cake of yarn does not shrink subsequently, and denier changes are cut to a minimum. The improvement in the softness of the yarn is marked, as shown in Table III.

(E) The fiber was then passed into the centrifuge pot. Cakes have been collected in runs of 6 hours without a break. At pot speed, spinning speeds of 65 meters/minute have been attained.

(F) The cake of yarn from the pot may be stored for several hours to complete the formaldehyde reaction, in which case the bound formaldehyde will be about 2 percent. If greater formaldehyde uptake is desired, additional treatment in a 30 percent sodium acetate-5 percent formaldehyde bath at pH 6 is used. The major beneficial effects of formaldehyde are increases in wet tenacity and in flexibility. Formaldehyde treatments at high acidities have been reported to produce boil-stable cross-linkages [14, 4] but we have not observed such an effect. The fiber is ordinarily washed in tap water and dried at 100°F.

(G) Of the many methods we have tested of stabilizing the fiber to boiling acid dye baths, acetylation is the best. This method, which is used commercially [1], was the subject of an earlier study in this laboratory [2]. There are marked deviations in the behavior of the highly stretched fiber here described from that of the low-tenacity fiber investigated previously. Moisture content of the fiber is important, for acetic acid exerts a deleterious effect on the dry strength of the fiber. (See Table IV.) Experiments with fibers of different water contents showed a similar effect.

Complete stabilization of the fiber to acid dye baths is not attained by this procedure, but the fiber can be

TABLE IV. ACETYLATION OF CASEIN FIBER FOR 1 HOUR AT 88°C WITH ACETIC ACID AS A CATALYST

Acetylating solution*	Tenacity at 70°F, 65% R.H. (g./den.)
Control	1.10
8% Ac_2O , 0% HOAc	1.09
8% Ac_2O , 2% HOAc	0.98
8% Ac_2O , 4% HOAc	0.93
8% Ac_2O , 6% HOAc	0.92

* 86-92% petroleum ether, b.p. 88°C, was used as a diluent.

treated with substantive dyes for 1 hour at 80°C without loss of tenacity. Other stabilizing treatments are being investigated.

Interesting results were obtained with a commercial-grade silicone halide containing 25 percent of hydrolyzable chlorine. The casein yarns, which contained about 10 percent of moisture at the start of the treatment, were boiled in a 1-percent silicone halide solution at the reflux temperature of the petroleum ether solvent, which was 38°C. The yarn was centrifuged, dried, and then baked at 120°C for 10 minutes. The minimal result was the raising of the dry strength of the yarn as well as the wet strength. The vapor-phase water absorption of the treated yarn 1018, measured by Dr. E. F. Mellon, was found to be unchanged from the original value. The yarns can be dyed after this treatment. (See Table V.)

Evaluation and Discussion

The fiber finished by acetylation has some noteworthy properties, which are due in large part to the fiber's high breaking elongation. The load-elongation curves obtained with a Scott I-P-2 Serigraph show

TABLE V. EFFECT OF SILICONE TREATMENT ON TENACITY

Treatment	Tested at 70°F, 65% R.H.		Tested wet	
	Tenacity (g./den.)	Elongation (%)	Tenacity (g./den.)	Elongation (%)
Yarn 1018				
Reflux in 1% solution	1.27	50	0.68	50
	1.23	50	—	—
Untreated control	1.09	50	0.50	50
Yarn 1020				
Reflux in 1% solution	1.33	45	0.59	50
Untreated control	1.11	45	0.40	45

TABLE VI. PROPERTIES OF 150-FILAMENT, 300-DENIER YARN

Fiber	Tested at 70°F, 65% R.H.		Tested wet		Toughness* index (g./den.)	Stiffness† (g./den.)	Elasticity‡ (%)
	Tenacity (g./den.)	Elongation at break (%)	Tenacity (g./den.)	Elongation at break (%)			
"Raw"	1.2	50	0.56	45	0.30	2.4	4.5
Acetylated	1.0	50	0.49	45	0.25	2.0	3.2
Rayon 100/300	2.2	22	1.1	30	0.24	10.0	3.2

* Area under stress-strain curve to break; $\frac{\text{tenacity} \times \text{elongation } \%}{200}$.

† $\frac{\text{Tenacity} \times 100}{\text{Elongation, } \%}$.

‡ Elongation at the yield point.

distinct reinforcement during the flow process in the dry fiber. Flexibility as measured by knot strength is high. Regain of the fiber is about 14 percent, and the heat evolved on wetting the fiber contributes to the warm feel characteristic of wool. The fineness and the absence of scale structure give it silklike characteristics as well. The fiber evaluation indices of Dr. H. DeW. Smith [10] have been used to evaluate the fiber further. (See Table VI.)

A single-fiber autographic tester made by the Harris Instrument Company has been used to supply further data on the elastic properties of the yarn at low elongations. L. G. Ray [9] had previously noted the high resilience of casein fibers at low elongations. By stretching the fiber at a rate of 1.6 percent elongation per minute to various elongations and then permitting it to recover at the same rate, a more accurate comparison could be made between rayon and casein fibers. The area under the returning part of the curve, or the work recovered, expressed as a percentage of the work required to stretch the fiber to the given elongation, is compared for casein and rayon. (See Table VII.)

Further recovery of the yarn will take place after the load has been completely removed. The similarity of the casein yarn to wool is shown further by the correspondence of the loading and recovery behavior in water. Essentially complete recovery from elongations up to 30 percent is obtained. This property has

been observed by Wormell [13]. Since these curves are more responsive to methods of chemical stabilization, they are a means of readily evaluating such treatments [7, 12]. The field of usefulness for continuous-filament casein yarn, as well as the other contemporaneous protein fibers, will be increased by improvements in stability to textile processing.

Recent studies with model compounds have given evidence of the method by which formaldehyde forms cross-linkages in proteins [5]. Since the bridge between amide and amino groups is acid-labile, some of the cross bonds in casein fiber will be removed in acid dye baths. The chemical individuality of casein is such that stabilizing treatments which are effective for other proteins are not necessarily applicable to casein fibers. This is a general principle, for it derives from the differences in composition and structure of the various proteins, as pointed out in a recent review [6].

The success of the pot-spinning process we have developed is based on rapid hardening with basic aluminum salts. Two British patents have been issued on pot-spinning processes [3]. The first avoids the shrinkage difficulty by relaxing the fiber before it enters the pot. The second makes use of a hot-air blast to dry the tow as it enters the centrifuge. The properties of the fiber produced by these processes have not been reported.

Preliminary evaluation of the casein fiber in knitted and woven goods has been made. It has been successfully knitted on circular half-hose machines, and woven into fabrics which exhibit the unusual properties to be expected from such a fiber. It is still deficient in tenacity and resistance to acid dyeing conditions. Research on these and other factors is continuing.

TABLE VII. PERCENT WORK RECOVERY FOR CASEIN AND RAYON YARNS

Fiber	Stretch to elongation of:		
	1%	2%	3%
Casein 150/300	97	77	59
Rayon 40/150	71	36	32

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